4

OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT: N00014-90-J-1148

R & T Code 4132016

Design, Synthesis and Characterization of Novel Nonlinear Optical Polymers

Dr. Sukant Tripathy
University of Massachusetts Lowell
Department of Chemistry
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May 31, 1995

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

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GRANT Number: **N00014-90-J-1148**

GRANT Title: **Design, Synthesis and Characterization of Novel Nonlinear Optical Polymers**

Principal Investigator: Dr. Sukant Tripathy

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Part I

a. Number of papers submitted to refereed journals, but not published: **3**
b. Number of papers published in refereed journals (list attached): **8**
c. Number of books or chapters submitted, but not yet published: **2**
d. Number of books or chapters published (list attached): **0**
e. Number of printed technical reports & non-refereed papers (list attached): **6**
f. Number of patents filed(pending): **4**
g. Number of patents granted (list attached): **0**
h. Number of invited presentations (list attached): **10**
i. Number of submitted presentations(list attached): **5**
j. Honors/Awards/Prizes for contract/grant employees (list attached): **5**

k. Total number of full-time equivalent graduate students and post-doctoral associates supported during this period, under this R & T project number:

Graduate Students: 1
Post-Doctoral Associates: 1
including the number of,
Female Graduate Students: 0
Female Post-Doctoral Associates: 0
the number of,
Minority Graduate Students: 0
Minority Post-Doctoral Associates: 0
and the number of,
Asian Graduate Students: 1
Asian Post-Doctoral Associates: 1

Other funding (list agency, grant title, amount received this year, total amount, and the period of performance, and briefly state the relationship of that research to your ONR grant):

The research listed below is not related to the reported ONR grant.

Polaroid Corporation "*Demonstration of Optical Switching*" Research Grant, May 23, 1994 - August 30, 1994 - $80,000.00.

American Chemical Society/Petroleum Research Fund, "*Novel Photocrosslinked NLO Polymers and Related Electro-Optic Device*" Research Grant, January 1, 1992 - August 31, 1994 - $43,000.00

U.S. Army, Natick, " *Engineering of Proteins and Devices for Biosensor Applications*", Research Grant, April 1, 1993 - September 30, 1994 - $47,495.00.

Department of the Army, University Research Initiative, "*Intelligent Materials and Structures Based on Ordered Assemblies of DNA*" co-principal investigator with Professors Kenneth Marx and Jayant Kumar, Research Grant, March 15, 1993 - February 15, 1995 - $69,282.00.

Spire Corporation, "*Polymeric Materials for Second Harmonic Generations*" Research Grant, August 11, 1993 - April 15, 1995 - $60,000.00.

National Science Foundation, "*Interpenetrating Network Second Order Nonlinear optical Polymers*" Research Grant, March 1, 1994 to February 28, 1995, $80,000.00, and March 1, 1995 to February 29, 1996, $80,000.00.

Part II

a. Principal Investigator: Dr. Sukant Tripathy

b. Current telephone number: 508-458-7116

c. Cognizant ONR Scientific Officer: Dr. Kenneth J. Wynne

d. Brief description of the project.

The principal focus of the project is to develop new materials chemistry based on molecular level design and solid state chemistry. The goals have been to develop electroactive polymers with novel electronic, optical and nonlinear optical properties. Second and third order nonlinear optical materials have been developed based on conjugated macromolecules and asymmetric anharmonic molecular electronic dipolar oscillators.

In this multidisciplinary research effort, starting from first principle, bulk self assembly processing techniques needed to control the molecular and supermolecular organizations of optical and electroactive molecules have been developed. They include spontaneous molecular organization of nonlinear optically active conjugated polymers such as polydiacetylenes with conjugating and hydrogen bonding side groups. A series of new soluble PDAs of the same class with further functionalization, elaborating on the already defined design principle have been developed.

Large amplitude holographic surface relief gratings on azobenzene side chain polymer films have been optically produced without any subsequent processing steps. Upon exposure to an interference pattern of a visible laser beam, optically driven macro scale molecular motions lead to surface relief grating structures potentially applicable in various optical elements and optical devices

e. Significant results during last year.

1. A series of new soluble polydiacetylenes based on macromolecular self-assembly concept and process has been developed. The idea is to employ a NLO active chromophore (R1) as one of the substituents and a flexible, hydrogen bond forming moiety (R2) as the second substituent.

2. A new process of direct formation of holographic surface relief gratings with large surface modulation depth (> 1000 Å) has been developed based on polymer films containing azobenzene side chains. Trans-cis-trans photoisomerization of the azobenzene side groups leads to macro scale

molecular motions causing large surface modulation without subsequent processing steps. The gratings were stable at ambient conditions and the samples were reusable after erasing the gratings by heating the film above the glass transition temperature

f. Brief summary of plans for next years work

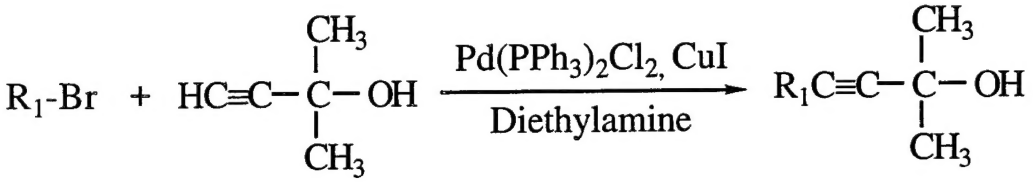
Molecular Systems Design and Synthesis: The bulk self assembly processing technique needed to control the molecular and supermolecular organizations of NLO active conjugated polymers such as polydiacetylenes, polythiophenes and poly(1,4-phenylene vinylene) derivatives with further functionalization, elaborating on the already defined design principle will be investigated. Synthetic schemes of the various polydiacetylenes, poly(1,4-phenylene vinylene) derivatives, and polythiophenes of interest are described in Schemes 1-3, respectively.

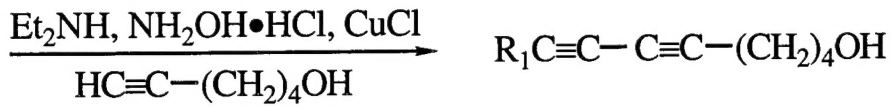
A series of polymers with various chromophore side groups and backbones will be synthesized and investigated to explore the mechanism of the surface relief grating formation process and consequently to optimize the materials and the process. Synthetic schemes of polymers with various chromophores and with varied backbone flexibility are described in Schemes 4-5, respectively.

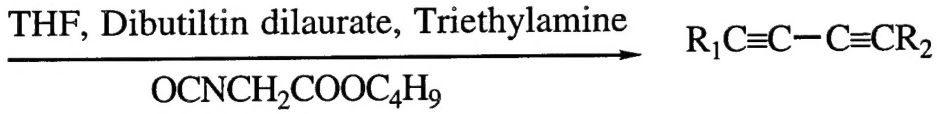
Processing and fabrication: No special technique or substrate is necessary for fabrication of these soluble conjugated polymers. Upon spin coating or casting from a solution, the polymer chains self organize in an acentric stable polar organization without recourse to poling.

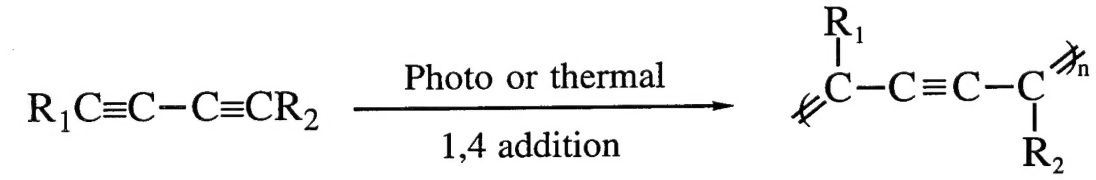
For surface grating study, polymer films will be produced by spin coating and LB techniques on various substrates such as glass, silicon, and mica etc. A simple interferometric apparatus will be used for the grating formation using various laser beams at visible range. The intensity, polarization and writing angles of laser beams will be varied and the effects will be investigated.

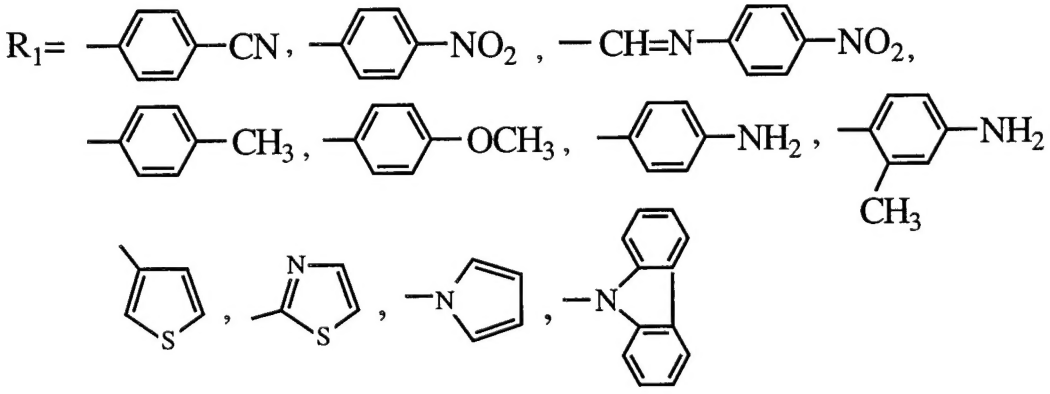
Characterization: Numerous solid state characterization techniques are being employed. Polarized FT-IR, FT-Raman, and UV-Vis-NIR spectroscopies will be utilized to investigate the alignment of the side groups of the polymer films. Other linear and nonlinear optical properties will be investigated. Dynamic mechanical analysis, dielectric measurements and thermal analysis will be carried out to study the molecular motion organization and property aspect. Photoconductivity and photovoltage will be measured. Electron microscopy study will be carried out to monitor the changes occurring in the crystal lattice during polymerization. Second and third harmonic generation are other properties of interest. Atomic force microscopy and electron microscopy will be employed for the surface characterization.





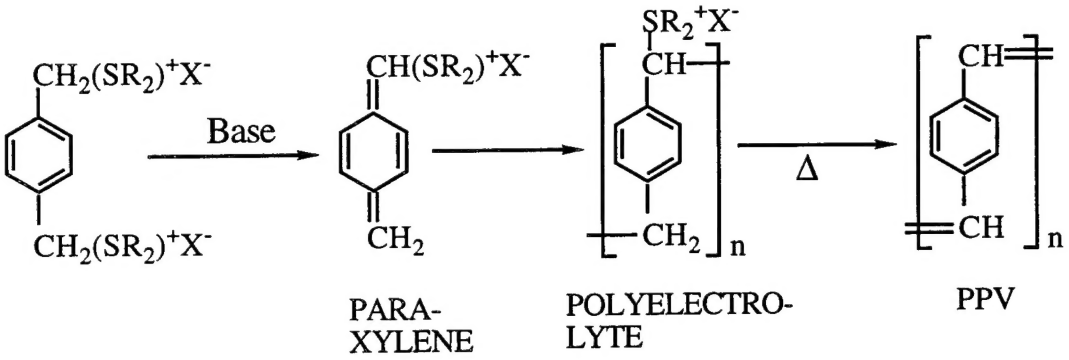




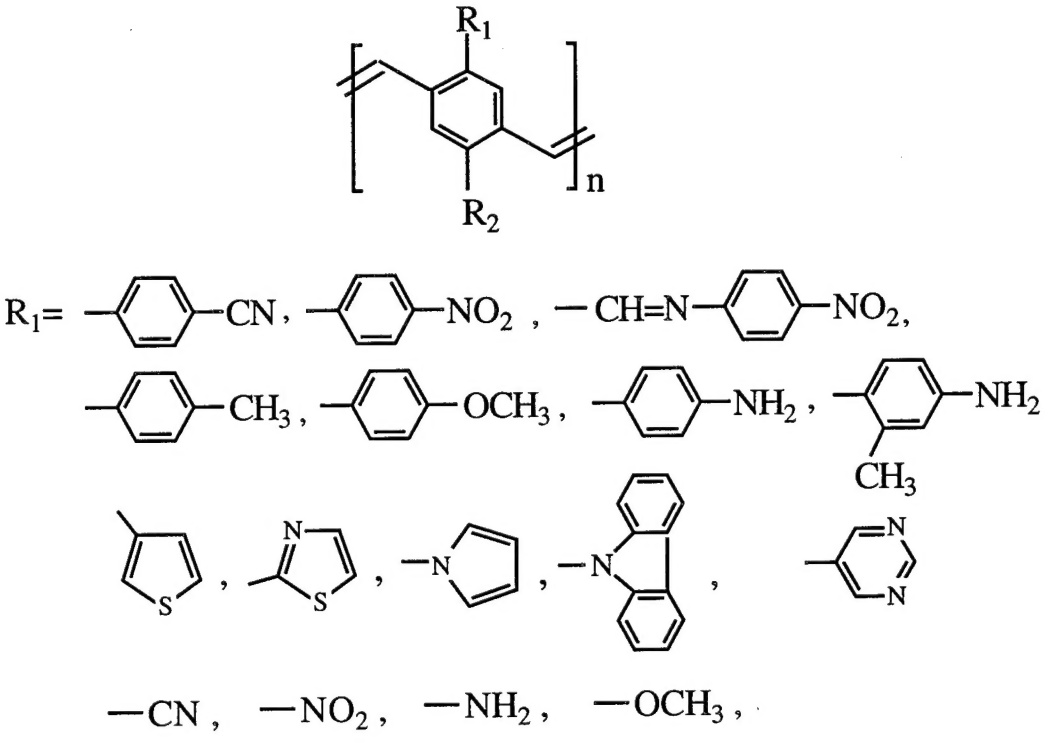


R_2= -$(CH_2)_n$OCONHCH$_2$COOC$_4$H$_9$ Where n=3-12

Scheme 1. Synthetic route to various polydiacetylenes proposed as new electro-optical materials.

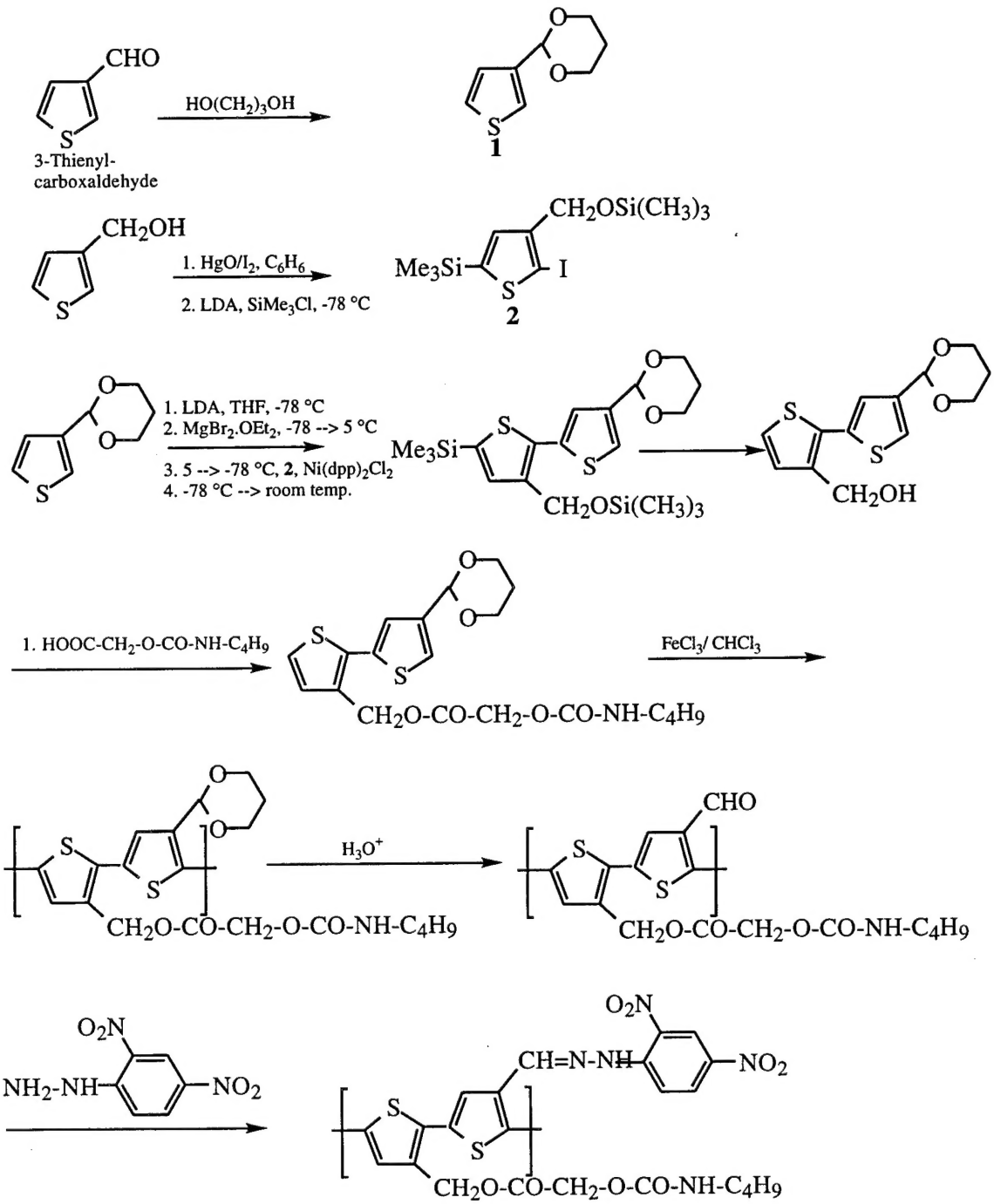


Wessling PPV synthesis

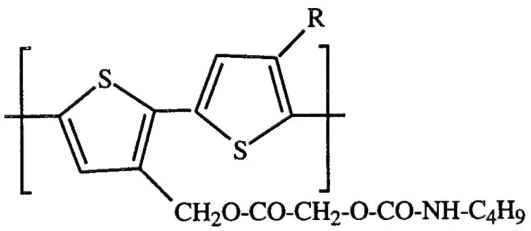


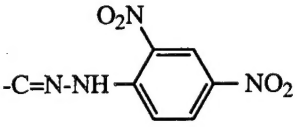
R_2= -$(CH_2)_n$OCONHCH_2COOC_4H_9 Where n=3-12

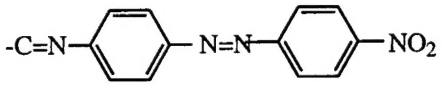
Scheme 2. Synthetic route to various poly(1,4-phenylene vinylene) derivatives proposed as new electro-optical materials (possible collaboration with Paul Lahti of UMass Amherst).

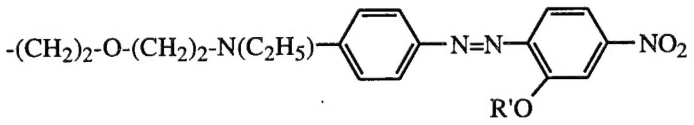


Scheme 3-A. Proposed route for the synthesis of asymmetrically substituted polythiophene derivatives proposed as new electro-optical materials.



R= 

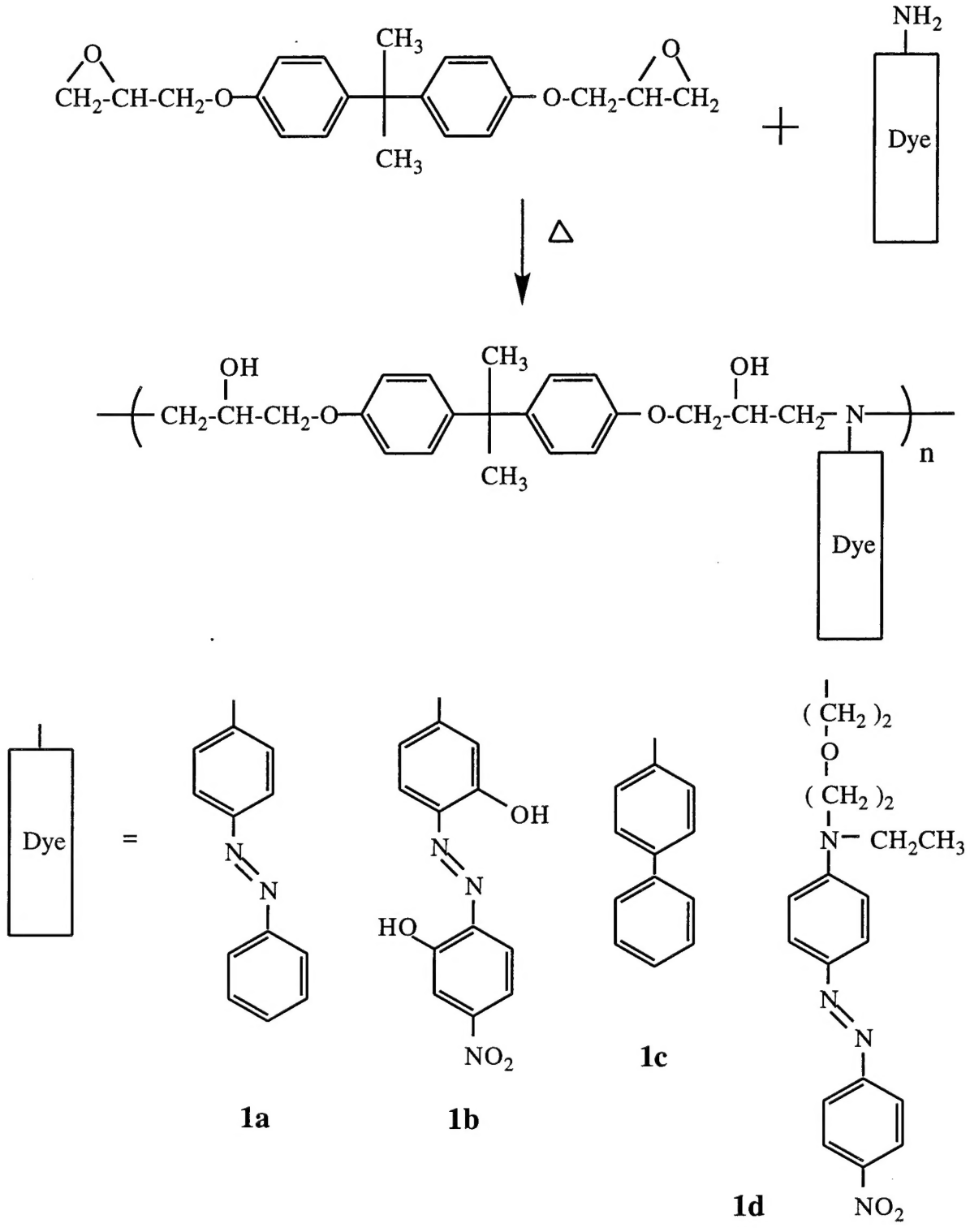




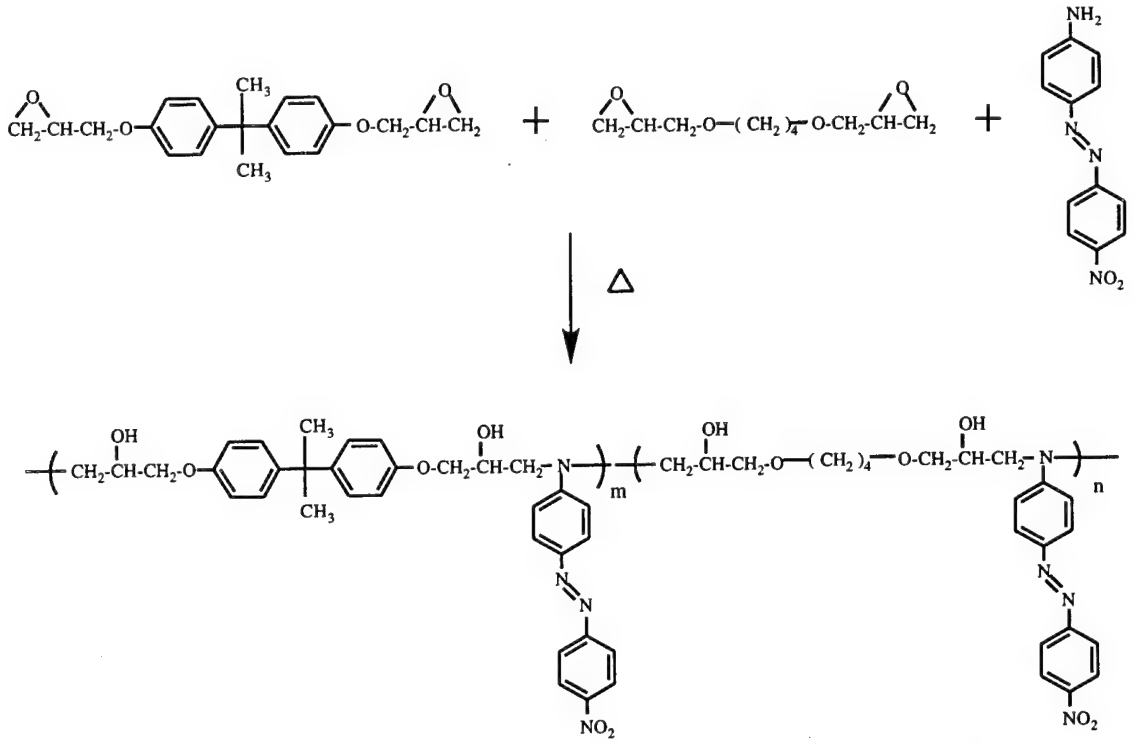
Where R' = C_6H_5-CH=CH-CO-

$CH_2=C(CH_3)$-CO-

Scheme 3-B. Various polythiophene derivatives proposed as new electro-optical materials. Continues from previous page.



Scheme 4. Proposed synthesis of the polymers with various dyes.



Scheme 5. Proposed synthesis of azo dye containing epoxy copolymers.

g. Name of graduate students and post-doctorals currently working on the project.

Post-doctoral Fellows
Dr. Woo Hong Kim.
Dr. Lian Li
Dr. Sutiyao Marturunkakul
Dr. Jeng-I Chen
Dr. Xiaogong Wang
Dr. Mario Cazeca

Graduate students (Ph.D. Candidates)	*Department*
Mr. Govindasamy Chittibabu	Chemistry
Mr. Dong Yu Kim	Chemistry
Xinli Jiang	Physics
Dong Wook Cheong	Chemistry
Richard Moody	Physics

Undergraduate students	*Department*
Mr. John Patronick	Chemistry

Part III

Research Highlights

Goal:

* To develop bulk self assembled conjugated polymers as second and third order nonlinear optical (NLO) materials.

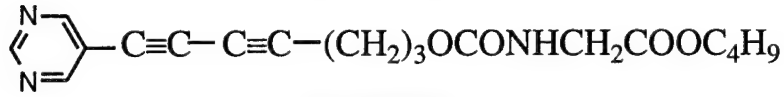
Approach:

* Conjugated polymers such as asymmetrically substituted polydiacetylenes are utilized as novel second and third order NLO materials.

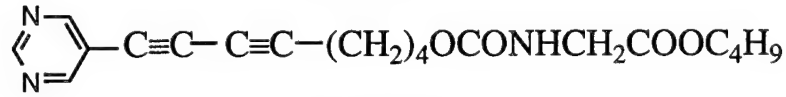
* Conjugating chromophore is further functionalized to increase the nonlinearity and a hydrogen bond forming polar, flexible moiety is employed to promote self organization and improved solubility.

Various PDAs synthesized in this work

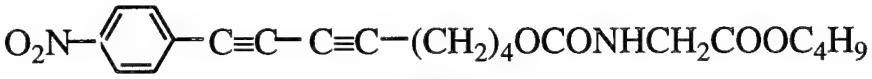
1-BPOD



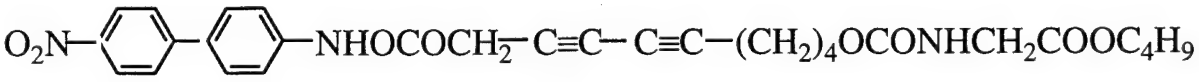
3-BPOD



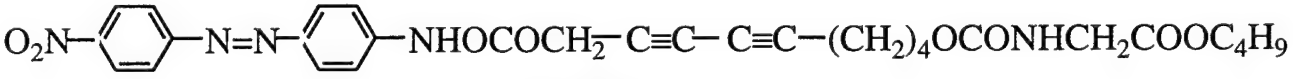
4-BPOD



NPOD

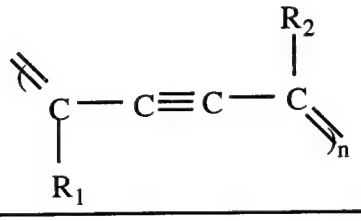


NBPD



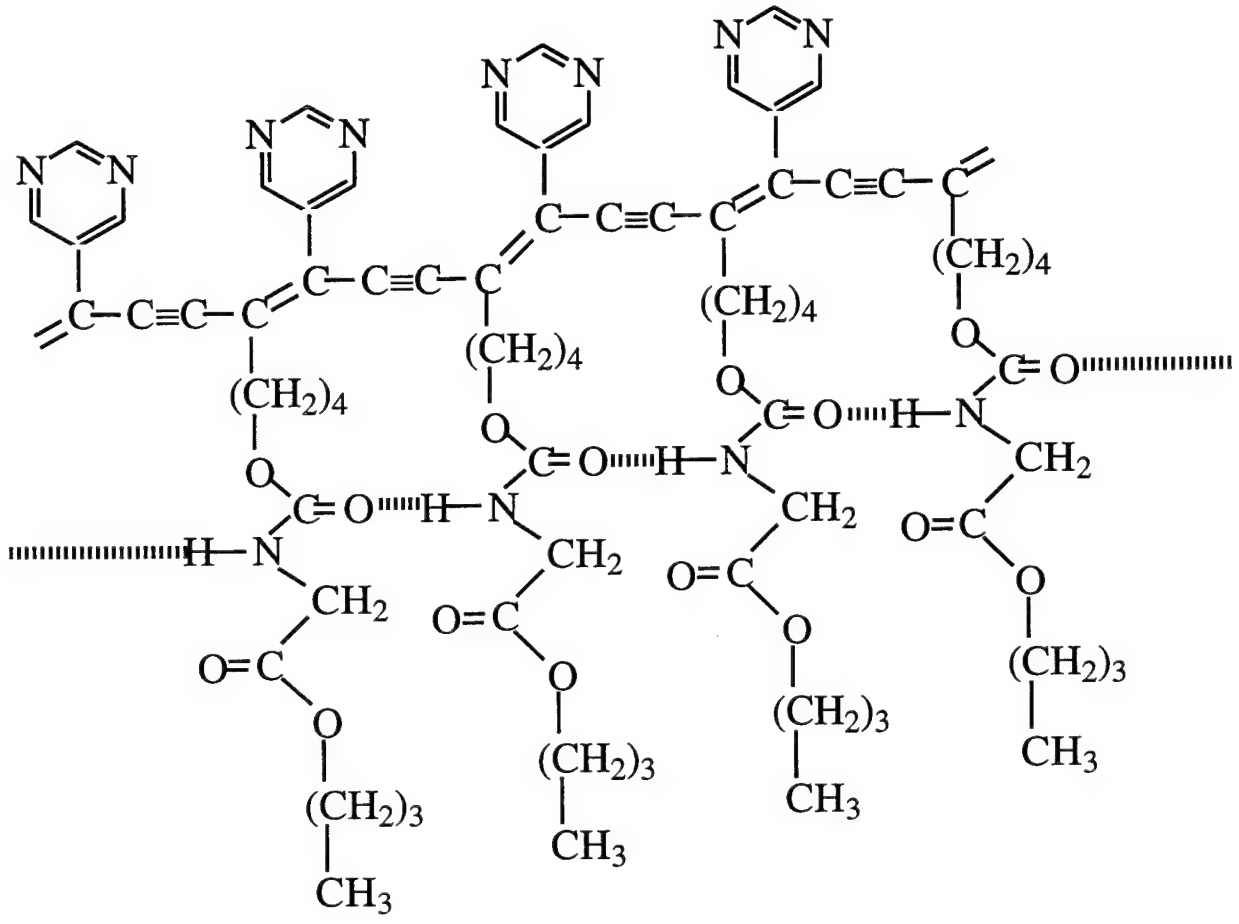
NABD

Solution properties of PDAs synthesized in this work



Polymers	Solubility			Absorption maximum (nm)	
	Chloroform	Phenol	TFA	Good solvent	Poor solvent
Poly(4-BPOD)	o	o	o	510	599
Poly(3-BPOD)	-	o	o	512	601
Poly(NPOD)	o	o	o	500	580
Poly(NBPD)	x	-	-	NA	NA
Poly(NABD)	x	-	-	NA	NA

Proposed hydrogen bonded network responsible for bulk self assembly in conjugated polymers

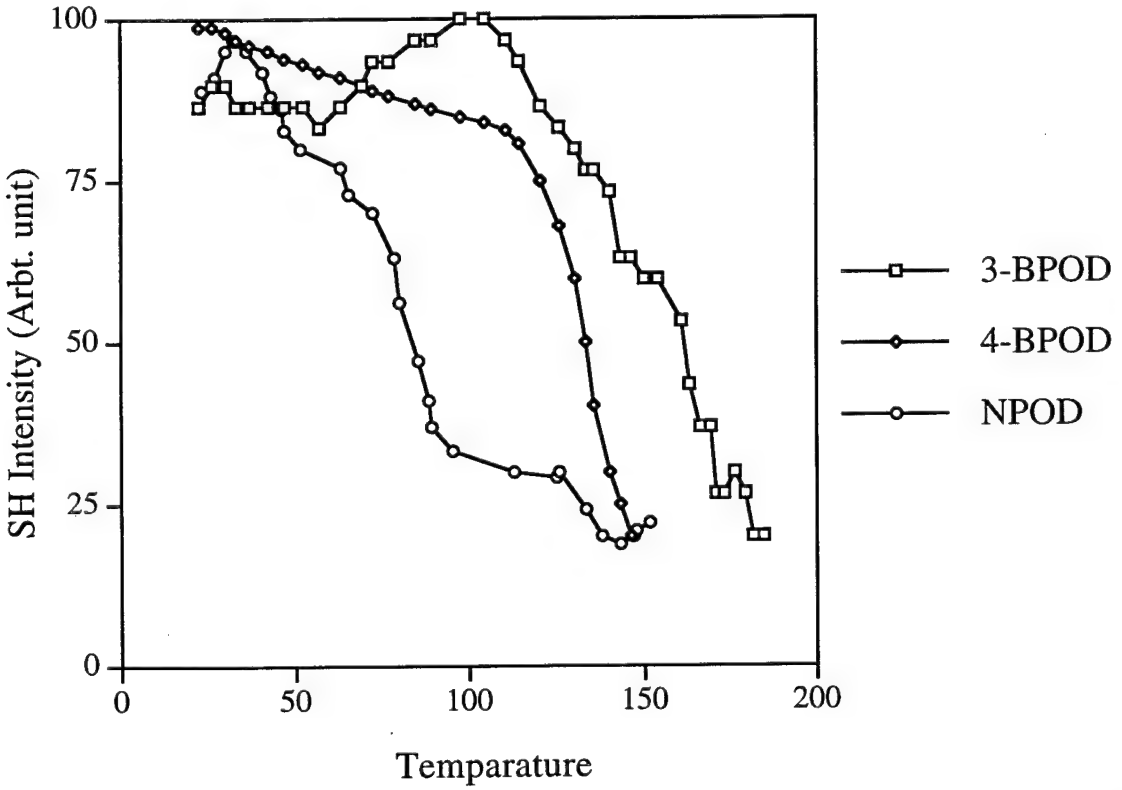


d33 values from spin coated films of various PDAs at incident wavelength of 1.06 μm.

Polymers	d33 (pm/V)	deff
Poly(3-BPOD)	0.5 - 2	·
Poly(4-BPOD)	3.32	·
Poly(NPOD)	0.7 - 4	·
Poly(NBPD)	23*	7.0
Poly(NABD)	NA	20

*: Obtained from LB films, NA: not available

$deff = (I^{2\omega}_{Urea} / I^{2\omega}_{Sample})$



Plot of second harmonic intensity vs. temperature from spin coated films of various PDAs.

Summary:

* A series of new soluble PDAs of the same class of poly(4-BPOD) with further functionalization, elaborating on the already defined design principle have been developed.

* The invention of this self assembling second order NLO polymer opens up numerous possibilities in molecular design for further optimization of properties.

Goal:

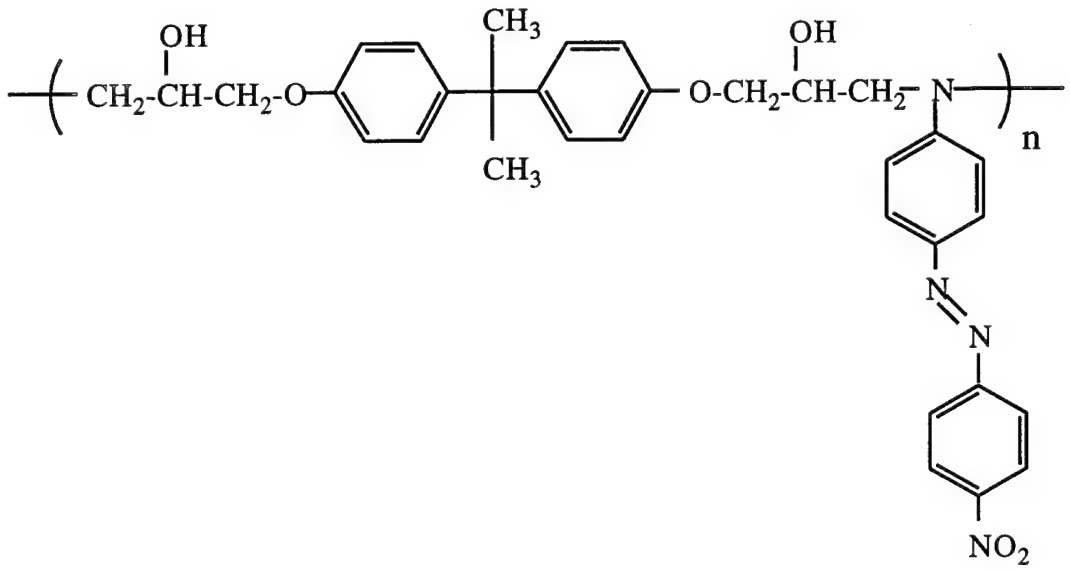
* To design and develop new reversible surface relief grating with large surface modulation depth directly produced on polymer films

Approach:

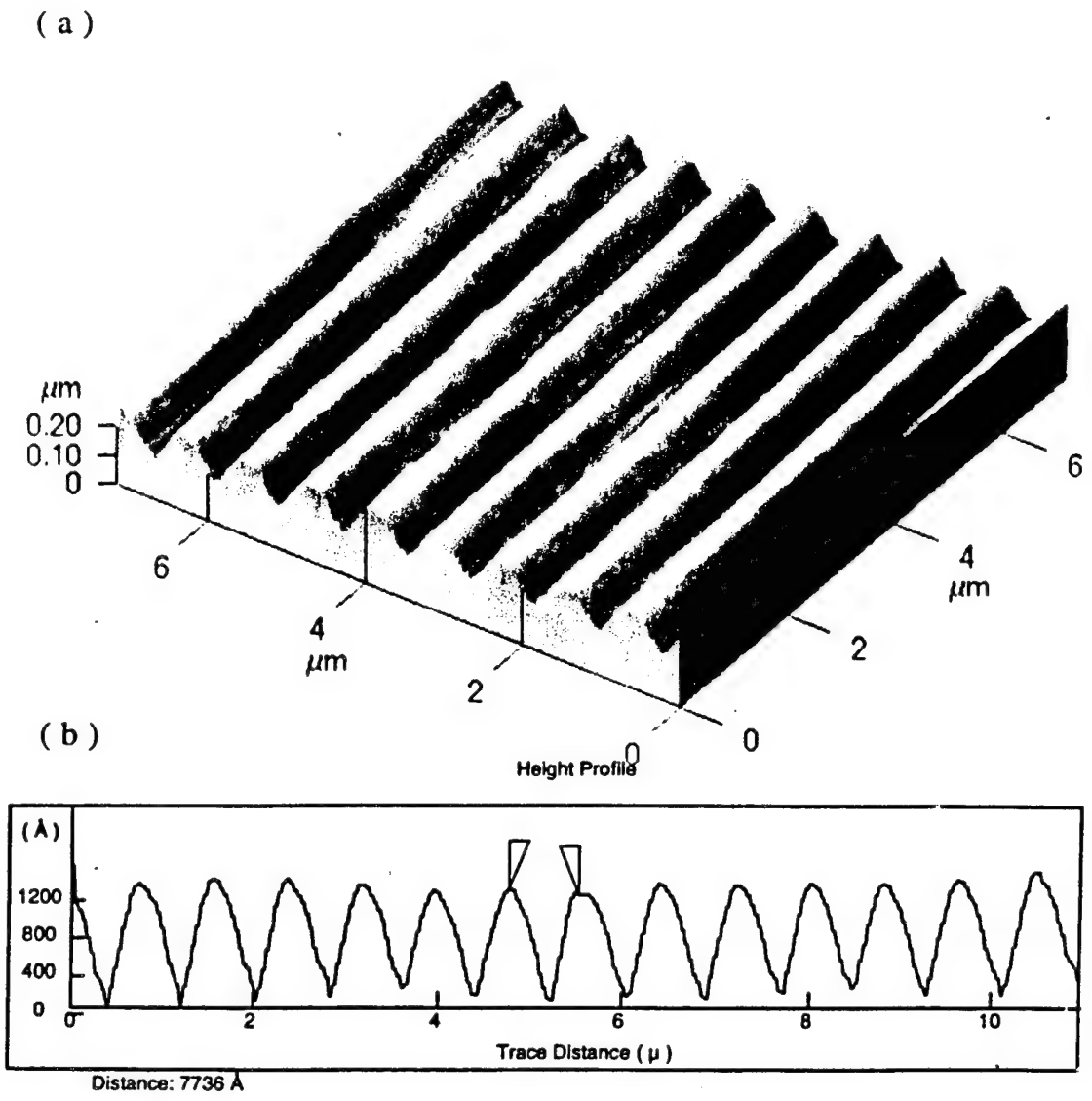
* Epoxy based polymers with azobenzene side chains were prepared.

* An interference pattern of a polarized Ar+ laser beam was exposed to the spin coated polymer films.

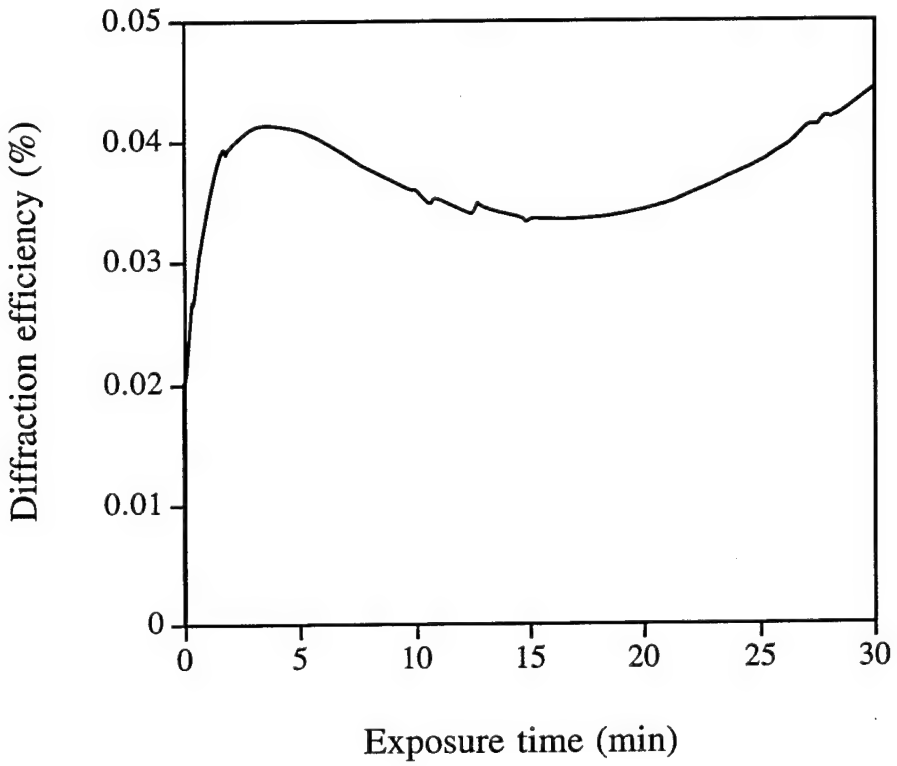
* Diffraction efficiencies were monitored and the surface of the films was investigated by AFM.



Chemical structure of the polymer PDO3.



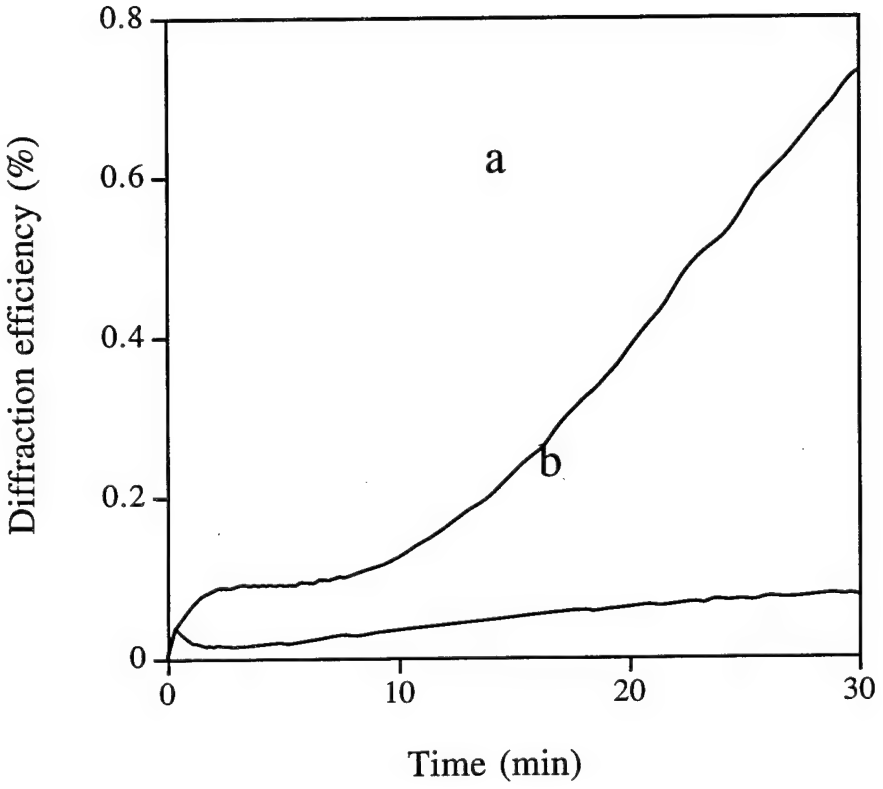
Atomic force microscopy of (a) three dimensional view and (b) profile of the surface relief gratings



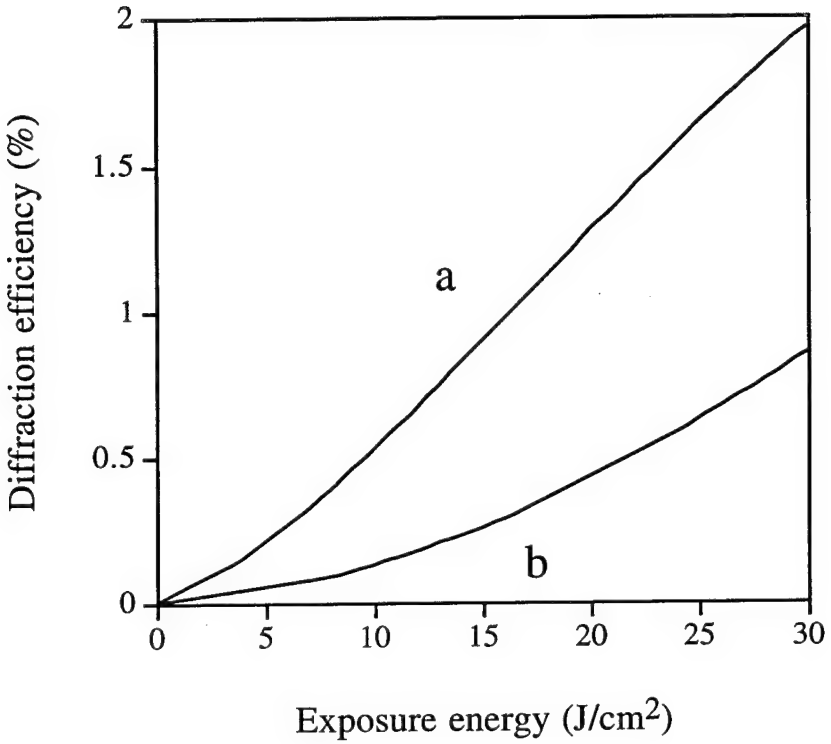
Diffraction efficiency of the film in the early stage with low intensity exposure.

* Orientation of the azobenzene groups was induced first and followed by surface deformation process.

* The diffraction efficiency of 30 % could be easily achieved.



Diffraction efficiency of the films exposed to (a) p-polarized beam and (b) s-polarized beam.



Effect of exposure intensity on diffraction efficiency of the films exposed to (a) 50 mW/cm2 and (b) 5mW/cm2.

* Thermal effect assists the surface deformation process

Summary:

* A new process of direct formation of large amplitude surface relief gratings on polymer films was developed. The surface gratings were stable at ambient conditions and erasable by heating the polymer above T_g.

* The surface modulation depth of more than 1000Å and the diffraction efficiency up to 30% could be achieved.

* Trans-cis-trans photoisomerization of the azobenzene side groups were responsible for the large scale surface deformation.

* The invention of this new direct process will provide numerous possibilities in design of new optical elements and devices.

b. Published Papers in Refereed Journals 8

1. "Relaxation study of poled nonlinear optical polymers by infrared reflection-absorption spectroscopy", (J.I. Chen, S. Marturunkakul, Y.M. Chen, J. Kumar and S.K. Tripathy) *European Polymer Journal* 30 (12) pp.1357-1362 (1994).

2. "Novel polydiacetylenes with chromophoric substituents: materials for second and third order nonlinear optics", (C. E. Masse, W. H. Kim, K. VanderWiede, J. Kumar, S. K. Tripathy), *Molecular Crystals Liquid Crystals,* Vol. 256 November, (1994).

3. "Low loss second-order nonlinear optical polymers based on all organic sol-gel materials" (R. J. Jeng, G. H. Hsiue, J. I. Chen, S. Marturunkakul, L. Li, X. L. Jiang, R. A. Moody, C. E. Masse, J. Kumar, and S. K. Tripathy) *Journal of Applied Polymer Science* Vol. 55 pp 209-214 (1995).

4. "An interpenetrating polymer network for second-order nonlinear optics", (L. Li, J. I. Chen, S. Marturunkakul, J. Kumar, S. K. Tripathy),*Optics Communications*, 116, 421-424 (1995).

5. "Photoconduction in a polydiacetylene film", T. Ravindran, W. H. Kim, A. K. Jain, J. Kumar, S. K. Tripathy, *J. Phys.: Condens. Matter* 6 1994.

6. "Self assembled asymmetrically substituted polydiacetylene as a novel second order NLO material", S. K. Tripathy, W. H. Kim, B. Bihari, R. Moody and J. Kumar, *Synthetic Metals*, 71, 1675, 1995.

7. "Self assembled spin coated and bulk films of a novel polydiacetylene as second order nlo polymers", W. H. Kim, B. Bihari, R. Moody, N. B. Kodali, J. Kumar, and S. K. Tripathy, *Macromolecules* 28, 642 1995.

8. "Laser -induced holographic surface relief gratings on nonliniear optical polymer films", D.. Y. Kim, L. Li, J. Kumar, and S. K. Tripathy, *Appl. phys. lett.*, 66, 1166, 1995.

e. Printed Technical Reports/Nonrefereed Papers 6

1. "Novel polydiacetylenes as materials for second and third order nonlinear optics" (W.H. Kim, C.E. Masse, B. Bihari, S.K. Tripathy, and J. Kumar) *Electrical, Optical, and Magnetic Properties of Organic Solid State Materials,* A. Garito, A. Jen, L. Dalton, C. Lee, Eds.; MRS Proceedings Vol. 328 667-72 (1994).

2. "Self assembled spin coated films of asymmetrically substituted polydiacetylene as second order NLO polymers", S. K. Tripathy, W. H. Kim, B. Bihari, R. Moody and J. Kumar, *IUPAC International Symposium Proceeding,* Functional and High Performance Polymers, 1994, 6A-02-IL, 65.

3. "Diacetylenes for second and third order nonlinear optics", C. E. Masse, W. H. Kim, X. L. Jiang, J. Kumar, and S. K. Tripathy, *IUPAC International Symposium Proceeding*, Functional and High Performance Polymers, 1994, 6A-04, 69.

4. "Novel organic sol-gel materials for second order nonlinear optics", R.J. Jeng, G.H. Hsiue, J.I. Chen, S. Marturunkakul, L. Li, X.L. Jiang, C. Masse, J. Kumar, and S.K. Tripathy, In *Electrical, Optical and Magnetic Properties of Organic Solid State Materials*; A.F. Garito, A. K-Y Jen, L.R. Dalton, and C. Y-C Lee, Eds.; MRS Sym. Proc. Vol. 328; Material Research Society: Pittsburgh, 1994, pp 583-588.

5. "Polyimide/inorganic composite-interpenetrating polymer network for stable second order nonlinear optics", S. Marturunkakul, J.I. Chen, L. Li, X.L. Jiang, R.J. Jeng, J. Kumar, and S.K. Tripathy, In *Electrical, Optical and Magnetic Properties of Organic Solid State Materials*, A.F. Garito, A. K-Y Jen, L.R. Dalton, and C. Y-C Lee, Eds.; MRS Sym. Proc. Vol. 328; Material Research Society: Pittsburgh, 1994, pp 541-546.

6. "Polymers for second order nonlinear optical applications", S. K. Tripathy, J. Kumar, S. Marturunkakul, J. I. Chen and L. Li, SPE/ANTEC Proceedings, 1995, 53, 1611.

h. Invited Presentations 10

1. "Self assembled asymmetrically substituted polydiacetylene as a novel second order nonlinear optical material", S. K. Tripathy, W. H. Kim, B. Bihari, R. Moody and J. Kumar, ICSM, Korea, August, 1994.

2. "Interpenetrating polymer networks as stable second order nonlinear optical materials", J. Kumar, L. Li, J. I. Chen, S. Marturunkakul, S. K. Tripathy, CEOT Conference, Bangalore, India, July 23, 1994.

3. "Polymers for photonics", S.K. Tripathy, Queens University, August 6, 1994.

4. "Photopolymers and applications in holography, optical data storage, optical sensors, and interconnects", L. Li, K.G. Chittibabu, J. Kumar, S. K. Tripathy, SPIE Proceedings August 16-18, Quebec, Canada., 1993.

5. "Stable second order nonlinear optical materials based on interpenetrating polymer network", S. Marturunkakul, J. I. Chen, L. Li, X.L. Jiang, R. J. Jeng, S. Kamtekar, J. Kumar, S. K. Tripathy, OSA/ACS Fall Meeting, Symposium on Polymeric Thin Films for Photonic Applications, Washington, DC, August 20-24, 1994.

6. "Design of new polydiacetylenes as self assembling second order nonlinear optical polymers", W. H. Kim, X. L. Jiang, J. Kumar, and S. K. Tripathy, IUPAC, Taiwan, November 1994.

7. "Diacetylenes for second and third order nonlinear optics", C. E. Masse, W. H. Kim, X. L. Jiang, J. Kumar, and S. K. Tripathy, IUPAC International Symposium, Functional and High Performance Polymers, Taiwan, November, 1994.

8. "Photovoltaic devices from C_{60} and polythiophene", S. Tripathy, Materials Research Society Symposiumn on Science and Technology of Fullerene Materials, Boston, MA, Nov. 30, 1994.

9. "Photonic polymers from first principle", Symposium on Photonic Materials entitled "New Horizons in Photonic Materials", University of Louisiana, Baton Rouge, LA, Sukant Tripathy, February 25, 1995.

10. "Polymers for second order nonlinear optical applications", S. K. Tripathy, J. Kumar, S. Marturunkakul, J. I. Chen and L. Li, SPE/ANTEC, Symposium on Electrical and Electronic Joint with Engineering Properties and Structure-Electroactive/Electrooptic Polymers, Boston, MA, May 8, 1995.

i. Submitted Presentations 5

1. "A structural characterization of diacetylene single crystal during polymerization: a transmission electron microscopy study", W. H. Kim, C. M. Sung, D. Y. Kim, H. Wang, J. Kumar, and S. K. Tripathy, Materials Research Society (Symposium Q 2.9), Boston, MA, November, 1994 .

2. "Photoinduced reversible holographic grating formation in nonlinear optical polymer films", D. Y. Kim, Lian Li, W. H. Kim, J. Kumar, and S. K. Tripathy, Materials Research Society (Symposium Za 8.3), Boston, MA, November, 1994 .

3. "Self assembled spin coated films of asymmetrically substituted polydiacetylene as second order nonlinear optical polymers", S. K. Tripathy, W. H. Kim, B. Bihari, R. Moody and J. Kumar, IUPAC International Symposium, Functional and High Performance Polymers, Taiwan, November, 1994 .

4. "Self assembled asymmetrically substituted polydiacetylene as a novel second order nonlinear optical material", W. H. Kim, J. Kumar, and S. K. Tripathy, American Chemical Society, Polymer Materials Science and Engineering Symposium. Washington D.C. USA, August, 1994 .

5. "Characterization of ultrathin asymmetric polydiacetylene films by atomic force and transmission electrom microscopy", D. W. Cheong, V. Shivshankar, H. C. Wang, C. M. Sung, J. Kumar,.S. K. Tripathy, Presented at Materials Research Society Spring Meeting, San Francisco, April 20, 1995.

j. Honors/Awards/Prizes 5

1. Sukant Tripathy was promoted to Provost and Vice Chancellor for Academic Affairs at the University of MassachusettsLowell, April, 1994.

2. Sukant Tripathy was a member of Massachusetts' delegation to India with Governor William Weld, for the development of international trade relations and educational and cultural exchange.

3. The 1995 Award for Outstanding Post Doctoral Associate was received by Dr. Woohong Kim of the Center for Advanced Materials and the Department of Chemistry at the University of Massachusetts Lowell for his contributions in the field of Chemistry

4. The 1995 Award for Outstanding Graduate Student in Polymer Science was received by K. G. Chittibabu of the Center for Advanced Materials and Department of Chemistry at the University of Massachusetts Lowell for his excellent scholarship in the field of Polymer Science.

5. Honorable Mention was awarded to Mr. Dong Yu Kim for his participation in the 1995 Student Paper Contest sponsored by SPIE- New England Chapter, and the Center for Electromagnetic Materials and Optical Systems, University of Massachusetts Lowell, May 19, 1995.